distilled to give **44** (39 g, 84% yield). The product gave only one peak by glc analysis. The H′ nmr spectrum consisted of the sharp singlet for $SiCH_3$, τ 9.96, a triplet for NCH_2, 7.53, and complex absorptions from 8.3 to 9.7.

This product (28 g, 0.1 mol) with ammonium chloride (5 g, 0.1 mol) was heated to reflux in 100 ml of benzene for 24 hr. The solution was permitted to cool slowly and crystals of the amine hydrochloride formed in 68% yield, mp 175-176.5°.

***N*-(3-Pentamethyldisiloxanylpropyl)aniline (46)**.—*N*-Allylaniline and pentamethyldisiloxane with chloroplatinic acid treated as above gave **46** in 75% yield.

1,3-Bis(3-dimethylaminopropyl)tetramethyldisiloxane (48).—To 50 ml of refluxing xylene that contained 10^{-4} mol of $H_2PtCl_6 \cdot 6H_2O$ was added a solution of 1,1,3,3-tetramethyldisiloxane (134 g, 1 mol) in dimethylallylamine (170 g, 2 mol). A rapid exothermic reaction occurred. When it subsided, the solution was distilled. About 20 ml as a precut was impure $HSiMe_2OSiMe_2(CH_2)_3NMe_2$ followed by **48** (233 g, 77% yield).

1,3-Bis(3-trimethylaminopropyl)tetramethyldisiloxane Dichloride (50).—1,3-Bis(3-chloropropyl)tetramethyldisiloxane (345 g, 1.2 mol) and trimethylamine (285 g, 4.8 mol) were heated together for 65 hr at 150° in an autoclave. The vessel was then cooled and opened to let excess trimethylamine evaporate. The residue was 463 g of sparkling white crystals (95% yield).

Bis-1,3-(3-*n*-butylaminopropyl)tetramethyldisiloxane (52).—*n*-Butylallylamine (20 g, 0.18 mol) and 1,1,3,3-tetramethyldisiloxane (12 g, 0.09 mol) were heated together to 103°, when one drop of 0.1 *N* $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol was added. The temperature quickly rose to 185°. The product was distilled to give **52** (22.5 g, 67% yield).

1,3-Bis(3-*N*-morpholine-2-methylpropyl)tetramethyldisiloxane (53).—1,3-Bis(3-chloro-2-methyl)tetramethyldisiloxane (98.8 g, 0.314 mol) was added to refluxing morpholine (300 g, 3.44 mol) and refluxed for 13 hr. The solution was then cooled. Morpholine hydrochloride precipitated and was filtered off. The filtrate was distilled to give **53** (98 g, 75% yield).

Registry No.—**1,** 31024-74-5; **2,** 18187-14-9; **3,** 31024-26-7; **4,** 13822-56-5; **5,** 18387-18-3; **6,** 18387-19-4; **7,** 31024-30-3; **8,** 3069-25-8; **9,** 31024-32-5; **10,** 31024-33-6; **11,** 31024-34-7; **12,** 31024-35-8; **13,** 18246-33-8; **14,** 18441-77-5; **15,** 31024-38-1; **16,** 31024-39-2; **17,** 3179-76-8; **18,** 31024-41-6; **19,** 2530-86-1; **20,** 3069-33-8; **21,** 3069-29-2; **22,** 1760-24-3; **23,** 31024-46-1; **24,** 919-30-2; **25,** 31024-48-3; **26,** 31024-49-4; **27,** 23410-40-4; **28,** 2530-82-7; **29,** 18037-12-2; **30,** 31024-53-0; **31,** 31024-54-1; **32,** 31024-55-2; **33,** 31024-56-3; **34,** 6044-50-4; **34** HCl, 31024-58-5; **35,** 31024-59-6; **36,** 31024-60-9; **37,** 5089-72-5; **38,** 18052-23-8; **39,** 31024-63-2; **40,** 3068-78-8; **41,** 31024-65-4; **42,** 31024-66-5; **43,** 31024-67-6; **44,** 31024-68-7; **44** HCl, 31024-69-8; **45,** 31024-70-1; **46,** 31024-71-2; **47,** 17907-36-7; **48,** 26526-97-6; **49,** 31020-47-0; **50,** 31020-48-1; **51,** 18547-06-3; **52,** 31020-50-5; **53,** 31020-51-6; **53** 2HCl, 31020-52-7.

Mechanism of the Reaction of Benzyl Alcohols with a Cyclic Trans Carbonate[1a]

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The mechanism of carbonate ring opening of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-carbonate (I) by various para-substituted benzyl alcohols in the presence of triethylamine was studied. The reaction is first order in both I and the amine-alcohol complex. The rate of carbonate ring opening was in the order $NO_2 > Cl$, $Br > H > CH_3$ for the para-substituted benzyl alcohols. This order correlates with the shift of the OH stretching frequency obtained when benzyl alcohol derivatives are complexed with triethylamine. The effect of solvent on the reaction rate of I with benzyl alcohol was determined for 16 solvents. Rate values correlate well with the hydrogen bonding and dielectric properties of the solvents.

Facile preparations of sugar trans carbonates[3] and their reactions with alcohols, mercaptans, and amines[4] prompted further investigation of these reactions. Our work[5] showed that methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2, 3-carbonate (I) reacted readily with primary and secondary amines. For reaction with thiols and alcohols to form the acyclic carbonates, a basic catalyst such as triethylamine was required.[5] In this paper we describe a study of (a) the mechanism of the amine-catalyzed reaction of the cyclic carbonate I with various para-substituted benzyl alcohols and (b) the effects of solvents of widely varying basicity and dielectric strength on this reaction.

Kinetics and Mechanism of the Reaction.—Preliminary rate comparisons of carbonate ring opening in I by benzyl alcohol, α-toluenethiol, and benzylamine at 100° in the presence of triethylamine are reported in Table I.

TABLE I

RATES OF CARBONATE RING OPENING OF I BY BENZYL ALCOHOL, α-TOLUENETHIOL, AND BENZYLAMINE AT 100°

	Mole ratio			
Nucleophile	Nucleophile	$(C_2H_5)_3N$	I	$t_{1/2}$,[a] min
Benzyl alcohol	4	7	1	210
α-Toluenethiol	4	7	1	111
Benzylamine	4	. . .	1	16

[a] $t_{1/2}$ = the time required for one-half of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-carbonate (I) to react.

Under the reaction conditions used, the order of reactivity is amine > thiol > alcohol and their ratio of half-life is 1:7:13. This order correlates with predicted nucleophilicities of these compounds.[6] The reaction

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(1) (a) Based in part of the M.S. thesis submitted by E. I. Stout to Bradley University, 1968, and presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13-18, 1969. (b) Northern Regional Research Laboratory. (c) Bradley University.

(2) This is a laboratory of the Northern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Ill. 61604. The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

(3) W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, **4**, 445 (1967).

(4) E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Tetrahedron Lett.*, 4481 (1967).

(5) W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, **11**, 321 (1969).

(6) Jerry March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968, p 288; J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

with benzyl alcohol was studied in greater detail to learn more about its mechanism because of long-range interests in conditions for reacting various hydroxyl compounds with sugar carbonates.

Rate measurements of carbonate ring opening were made on the system benzyl alcohol–I (4:1 molar ratio) in the presence of different amounts of triethylamine as catalyst. As plotted in Figure 1, the log absorbance of cyclic carbonate carbonyl *vs.* time gives straight lines, the slopes of which directly depend upon concentration of triethylamine. These results show the reaction under these conditions to be first order in cyclic carbonate I. The dependency of the reaction on amine can be explained by assuming the existence of a reactive complex formed between triethylamine and benzyl alcohol, which then reacts with I. If such a complex formation does occur between the alcohol and amine, the intensity of the "free" OH stretching absorption should decrease. This decrease indeed takes place.

Infrared analyses of xylene solutions of various para-substituted benzyl alcohols before and after addition of triethylamine reveal both a decrease in the free OH absorption and the appearance of a new peak (Table II).

TABLE II
HYDROXYL FREQUENCY SHIFTS OF TRIETHYLAMINE–PARA-SUBSTITUTED BENZYL ALCOHOL COMPLEXES AND THE HALF-LIFE OF THEIR REACTION WITH THE CYCLIC CARBONATE I

Para substituent[a]	Registry no.	ν_{OH}, cm^{-1}	$\nu_{complex}$,[b] cm^{-1}	$\Delta\nu$, cm^{-1}	$t_{1/2}$,[c] min
CH_3	31330-74-2	3620	3163	457	720
H	31330-75-3	3620	3160	460	480
Br	31330-76-4	3620	3150	470	222
Cl	31330-77-5	3620	3152	468	185
NO_2	31330-78-6	3620	3110	510	81

[a] All measurements in carbon tetrachloride at room temperature. [b] The OH stretching frequency of the triethylamine–alcohol complex. [c] The time required for one-half of I to be consumed in the reaction 0.20 *M* ROH + 0.05 *M* I + 0.12 *M* $(C_2H_5)_3N$, at 100° in xylene.

This new peak at a lower wavenumber is indicative of a hydrogen-bonded species such as would be found in an amine–alcohol complex.[7] Monitoring the free OH absorbance indicated that nearly complete equilibration was achieved in a few seconds. Values for $\Delta\nu$ were determined by subtracting the frequency of the OH absorbance values of the complex from the original frequency of the OH absorbance values. The concentration of the complex was measured by the decrease in absorbance at 3580 cm^{-1} after adding amine to the alcohol solution in xylene. Xylene solutions of the alcohol and amine–alcohol complex were heated to 100°, and I was added in amounts equivalent to the concentration of complex. The resulting reaction was monitored by measuring the decrease of the carbonyl absorption of the cyclic carbonate group of I at 1812–1840 cm^{-1}.

The rate constant, k, for the reaction should be given by $k = 1/t_{1/2}c_0$ where $t_{1/2}$ is the half-life of I and c_0 is the initial concentration of the amine–alcohol complex, if the reaction obeys the kinetic expression, rate $= k[\text{complex}][\text{I}]$. The rate constants summarized in Table III follow second-order kinetics for the reaction of five different para-substituted benzyl alcohols. The reaction can be represented by eq 1 and 2.

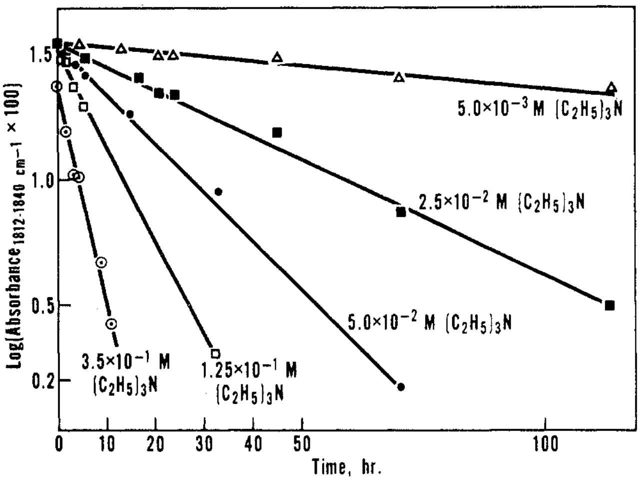
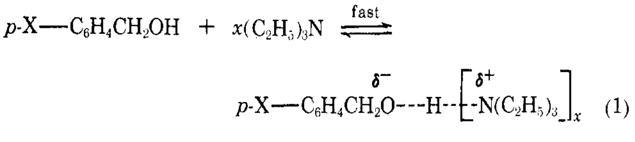
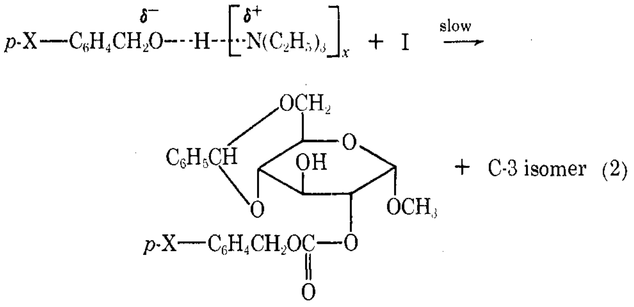


Figure 1.—Plot of log (absorbance $\nu_{1812-1840\ cm^{-1}}$ × 100) of trans carbonate I *vs.* time (hr) showing the effect of triethylamine concentration on the rate of reaction of 1.0 mmol of I with 4.0 mmol of benzyl alcohol in 20 ml of xylene at 100°.



$$p\text{-X—C}_6\text{H}_4\text{CH}_2\text{OH} + x(\text{C}_2\text{H}_5)_3\text{N} \xrightleftharpoons{\text{fast}} p\text{-X—C}_6\text{H}_4\text{CH}_2\overset{\delta-}{\text{O}}\text{---H--}\left[\overset{\delta+}{\text{--N}}(\text{C}_2\text{H}_5)_3\right]_x \quad (1)$$



(2)

The reaction rate sequence for the para-substituted benzyl alcohols is that expected based on increasing acidity of the hydroxyl hydrogen; *i.e.*, NO_2 > Br, Cl > H > CH_3. This order of reactivity is consistent with the strength of the complexes formed between the benzyl alcohols and triethylamine, as given by ν. The plot of $\Delta\nu$ *vs.* the rate of reaction (Figure 2) exhibits the correlation between stretching frequency of OH in the complex and rate of carbonate ring opening.

The spectroscopic data in Table II pose an interesting problem. Although OH absorbance frequencies for all five substituted benzyl alcohols are the same in carbon tetrachloride (3620 cm^{-1}) or in xylene (3580 cm^{-1}), the OH stretching frequencies of the alcohols when complexed with triethylamine differ considerably. The electrical effects of the para substituents of benzyl alcohol seem to be operative only when the molecule is complexed with the amine. This situation is in contrast to the well-recognized shift of the OH stretching frequency of benzoic acid and phenols in carbon tetrachloride as the para substituent is varied.[7] The hydroxyl absorbance frequency in benzoic acid is affected in weak complexing solvents by the electrical nature of the para substituents. On the other hand, Hojo,

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(7) J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954).

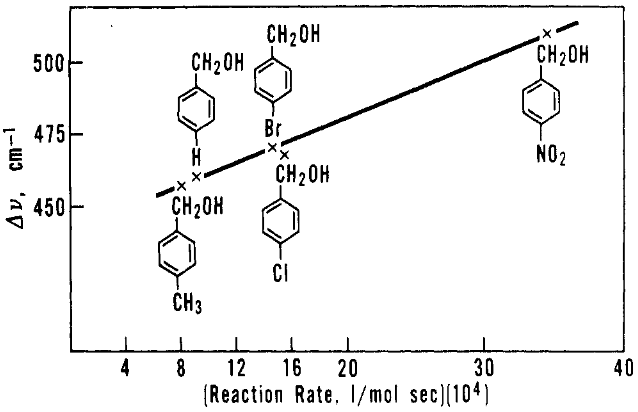

Figure 2.—Plot of OH stretching frequency of "free" alcohol minus OH stretching frequency of alcohol–amine complex ($\Delta\nu$) *vs.* rate of reaction of benzyl alcohol derivative with I in xylene at 100°.

TABLE III
RATE CONSTANTS FOR THE REACTION OF TRIETHYLAMINE–PARA-SUBSTITUTED BENZYL ALCOHOL COMPLEXES WITH CYCLIC CARBONATE I AT 100°

Para substituent	Complex, mol/l.	$t_{1/2}$, min		Rate constant × 10⁴, l./mol sec
CH_3	0.121[a]	168		8.20
	0.0835[b]	252		7.92
	0.0672[c]	308		8.05
	0.0392[d]	534		7.97
	0.0213[e]	960		8.15
			Av	8.05
H	0.127[a]	132		9.93
	0.0837[b]	204		9.97
	0.0743[c]	252		8.90
	0.0458[d]	444		8.20
			Av	9.20
Cl	0.130[a]	87		14.73
	0.103[b]	113		14.32
	0.0995[b]	114		14.70
	0.0880[c]	125		15.15
	0.0815[c]	126		16.23
	0.0510[d]	185		17.67
	0.0492[d]	200		15.27
	0.290[e]	360		15.97
	0.0257[e]	400		16.20
			Av	15.58
Br	0.143[a]	80		14.57
	0.102[b]	102		16.02
	0.0885[c]	126		14.95
	0.0555[d]	222		13.53
			Av	14.77
NO_2	0.144[a]	36		32.17
	0.142[a]	38		30.83
	0.105[b]	50		31.67
	0.0860[c]	51		38.00
	0.0845[c]	56		35.17
	0.0515[d]	81		40.00
			Av	34.67

[a] The complex was formed from xylene solutions which contained 0.2 *M* ROH and $(C_2H_5)_3N$ as 0.70 *M*, [b] 0.35 *M*, [c] 0.25 *M*, [d] 0.12 *M*, [e] 0.05 *M*.

Katsurakawa, and Yoshida[8] have reported that 1-naphthoic acid substituted at carbon 8 by Cl, Br, NO_2, and CH_3 gives essentially identical (3515–3530 cm^{-1}) OH stretching frequencies in carbon tetrachloride. This lack of electrical effect of para substituents in benzyl alcohol and of peri substituents in 1-naphthoic acid is being investigated.

Solvent Effects on Rate of Carbonate Ring Opening.—Two solvent parameters, (a) ability to form hydrogen bonds and (b) dielectric constant, were investigated for their effect on the rate of carbonate ring opening by benzyl alcohol. At some stage the opening of the carbonate must involve the transfer of a hydrogen from the amine–alcohol complex to the carbonate. The reaction rate should be influenced by the dielectric constant (ϵ) of the solvent, since the transfer of hydrogen should involve the creation of some degree of charge during the transition state. Therefore, the larger the ϵ of the solvent the faster the reaction if all other solvent properties remain constant.[9] Solvent basicity (ability to hydrogen bond) should also be significant but in a reverse manner. The greater the basicity of the solvent the greater should be its ability to complex with the alcohol, to lower the concentration of the amine–alcohol complex, and to yield a slower rate of reaction. This point can be illustrated by 3 and 4, in which S is the solvent:

$$C_6H_5CH_2OH + yS \rightleftharpoons C_6H_5CH_2O\text{---}H\text{---}S_y \qquad (3)$$

$$C_6H_5CH_2OH + x(C_2H_5)_3N \rightleftharpoons C_6H_5CH_2O\text{---}H\text{--}[\text{-}N(C_2H_5)_3]_x \qquad (4)$$

These two equations show that as the basic properties of the solvent (which is present in great excess over the amine) increase the amount of benzyl alcohol available for the amine–alcohol complex formation decreases. This decrease in the amine–alcohol complex concentration should have a direct effect on the rate of carbonate ring opening if the complex is involved in a rate-determining step in the reaction. The degree of interaction between the solvent and benzyl alcohol should be reflected in the strength of the hydrogen bond formed between the two. Ferguson[10] has pointed out that the formation of a hydrogen bond lowers the energy necessary to cause stretching. Therefore, when a hydroxyl group participates in hydrogen bonding, its infrared stretching frequency occurs at a lower frequency, which corresponds to the lower energy required. Fox and Martin[11] and also Badger and Bauer[12] have stated that a shift in the OH stretching frequency should be related to the strength of the hydrogen bond, and data of Widom, Philippe, and Hobbs[13] support this hypothesis. Therefore, in our study the frequency shift ($\Delta\nu$) for the OH group of benzyl alcohol in various solvents has been used to determine the basicity or the hydrogen-bonding ability of each solvent.

Values for $\Delta\nu$, tabulated in Table IV, were calculated by subtracting the OH absorbance frequency of benzyl alcohol in the various solvents from the absorbance frequency of the alcohol in carbon tetrachloride.

In Figure 3 the half-life of the reaction of I with benzyl alcohol catalyzed with triethylamine in different solvents has been plotted *vs.* the shift ($\Delta\nu$) of OH stretching frequency in that solvent. Since the ϵ of the solvent must be considered also, no order can be expected unless either $\Delta\nu$ or ϵ is held relatively constant

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(8) M. Hojo, K. Katsurakawa, and Z. Yoshida, *Tetrahedron Lett.*, 1497 (1968).

(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 347.

(10) L. N. Ferguson, "The Modern Structures of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, p 528.

(11) J. J. Fox and A. E. Martin, *Proc. Roy. Soc., Ser. A*, **162**, 419 (1937).

(12) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

(13) J. M. Widom, R. J. Philippe, and M. E. Hobbs, *J. Amer. Chem. Soc.*, **79**, 1383 (1957).

TABLE IV

SOLVENT EFFECT ON REACTION RATE OF BENZYL ALCOHOL WITH CYCLIC CARBONATE AT 70°

Solvent	ν_{OH}, cm^{-1}	$\Delta\nu$,[a] cm^{-1}	Dielectric constant, ϵ	Obsd $t_{1/2}$,[b] hr	Calcd $t_{1/2}$,[c] hr	$t_{1/2}$,[d] hr
Carbon tetrachloride	3617	0	2.2	1.8	1.8	1.8
Chloroform	3610	7	5.0	2.6	2.6	2.0
Toluene	3586	31	2.4	5.3	3.6	4.0
Xylene	3580	37	2.4	5.0	3.7	5.0
Nitrobenzene	3582	35	36.1	1.9	3.8	2.1
Benzyl ether	3570[e]	47	3.1	2.6	3.2	5.8
2-Butanone	3546	115	16.5	24	18.7	16.1
Cyclohexanone	3470	147	18.2	23	21.8	24.1
Tetrahydropyran	3443	174	6.6	30	32.6	40.7
Dioxane	3465	152	2.2	41	35.4	36.7
N,*N*-Dimethylformamide	3400	217	36.7	28.5	44.7	28.2
N,*N*-Dimethylacetamide	3380	237	38	34	42.4	29.2
Dimethyl sulfoxide	3325	292	45	28.5	21.8	23.7
N-Methylformamide	3310	307	171	0.29	0.36	1.3
N-Methylacetamide	3310	307	178	4.3	3.2	1.1
Pyridine	3255	352	12.5	30	28.6	31.8

[a] $\Delta\nu = \nu_{OH}$ in CCl_4/ν_{OH} in solvent used. [b] For reaction, cyclic carbonate I + benzyl alcohol + triethylamine (1:4:7 mmol ratio in 20 ml of solvent). [c] Calculated using eq 5. [d] Calculated using eq 6. [e] A signal at 3460 cm^{-1} was also observed.

as the other is varied. Comparison of solvents of similar $\Delta\nu$ shows that the reaction is faster in solvents of higher ϵ. For example, nitrobenzene (ϵ 36) gave a reaction rate about 2.4 times as fast as xylene or toluene (ϵ 2.4). Likewise, for dioxane (ϵ 2.2), tetrahydropyran (ϵ 6.6), and cyclohexanone (ϵ 18.2), the half-lives were in a ratio of 1.8:1.3:1. The rates of reaction in *N*-methylformamide and *N*-methylacetamide, two solvents of extremely high ϵ ($\sim$170), were much faster than for any other "basic" solvents.

If the solvents are grouped by ϵ, 0–30, 30–40, and $\sim$170, their half-life correlates with $\Delta\nu$. For solvents with ϵ of 0–30 (carbon tetrachloride, chloroform, toluene, xylene, 2-butanone, tetrahydropyran, pyridine, and dioxane), there is a reasonably linear relationship. Solvents of this group that have the largest deviation are dioxane and pyridine. Dioxane has two ether sites capable of hydrogen bonding with alcohol. This extra degree of hydrogen bonding should slow down the reaction which dioxane does. Pyridine also seems to give anomalous results in not being closer to the line with its high degree of basicity as measured by frequency shift and moderate dielectric constant. However, its basicity may be great enough so that it acts as a poor catalyst. At 100°, pyridine does catalyze the reaction of cyclic carbonate I with benzyl alcohol while the other solvents studied do not.

The data of Table IV have been correlated using an IBM 1130 computer with the aid of a multiple regression analysis program supplied by the IBM Corp.

Empirical eq 5–7, relating ϵ, $\Delta\nu$, and concentration (c), the molar concentration of solvent, have been calculated, where R^2 is the square of the correlation coefficient, n is the number of data points, and s is the antilog of the standard deviation of regression. In Table IV are the values calculated according to eq 5 and 6. The correlation studies indicated that for solvents of widely varying properties, the two parameters, $\Delta\nu$ and ϵ, are the most important ones in determining the reaction rate of benzyl alcohol with trans carbonate I.

$$t_{1/2} = (1.862)(1.124)^{(\Delta\nu c)}(0.908)^{(\Delta\nu c/10)^2}(0.981)^{(\Delta\nu c\epsilon/100)}$$
$$\begin{array}{ccc} R^2 & n & s \\ 0.958 & 16 & 1.40 \end{array} \qquad (5)$$

$$t_{1/2} = (1.862)(1.029)^{\Delta\nu}(0.9944)^{(\Delta\nu_2/100)}(0.9777)$$
$$\begin{array}{ccc} 0.839 & 16 & 1.93 \end{array} \qquad (6)$$

$$t_{1/2} = (1.610)(1.028)^{\Delta\nu}(0.9944)^{(\Delta\nu^2/100)}(0.9927^{(\Delta\nu\epsilon/100)}$$
$$\begin{array}{ccc} 0.828 & 16 & 1.98 \end{array} \qquad (7)$$

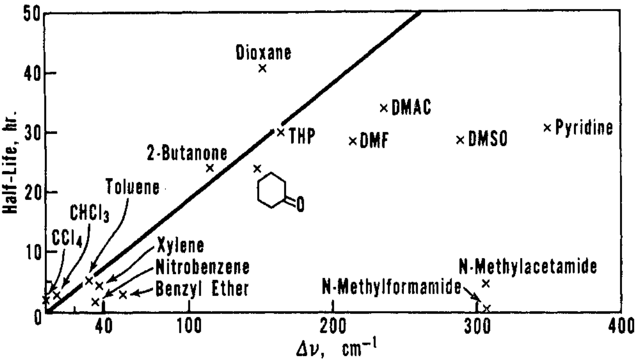

Figure 3.—Plot of the OH stretching frequency of benzyl alcohol in CCl_4 minus the OH stretching frequency in a different solvent ($\Delta\nu$) *vs.* the half-life of the reaction of benzyl alcohol with I catalyzed by triethylamine at 70°: DMSO = dimethyl sulfoxide, DMF = dimethylformamide, DMAC = dimethylacetamide, THP = tetrahydropyran.

Experimental Section

Determination of Complex Formation between Benzyl Alcohol and Triethylamine.—To 20.0 ml of xylene 4 mmol of benzyl alcohol was added and infrared spectrum was run against a xylene blank. The range 3000–4000 cm^{-1} was scanned on a Perkin-Elmer Model 621 spectrophotometer. After the desired amount of triethylamine was added, the spectrum was redetermined over the same wavelength range. The percentage difference in absorbance before and after addition of the amine was taken as the percentage of the original alcohol converted to the amine–alcohol complex. For example, in one determination the OH absorption at 3580 cm^{-1} decreased 46% in 15 sec on addition of 7 mmol of amine with no further change during the next hour. The wave numbers at maximum peak height were noted for both the alcohol and the amine–alcohol complex by rerunning the spectrum and reading the wavenumber counter.

Reaction of Amine–Alcohol Complex with I.—After concentration of the amine–alcohol complex was determined, the solution was warmed to 100° and an equal molar amount of I was added. The ensuing reaction was monitored by removing portions of the solution and recording the carbonyl absorbance for the cyclic carbonate at 1812–1840 cm^{-1} on a Perkin-Elmer Model 137 spectrophotometer at selected time intervals at room temperature.

The data were plotted and the half-life of the reaction was determined. Assuming second-order kinetics, the reaction rate was calculated for several different concentrations according to the formula $t_{1/2} = 1/kc_0$ where c_0 = initial concentration. In Table III, no corrections were made for change in the amine–alcohol equilibrium with temperature.

Solvent Effects on Reaction of I with Benzyl Alcohol–Triethylamine Complex.—To 20 ml of the solvent was added 0.432 g of benzyl alcohol. The infrared spectrum of this solution was recorded from 3000 to 4000 cm^{-1}. The position of the absorbance peak for the alcohol is shown in Table IV. This solution was treated with 1.00 ml of triethylamine and warmed to 70° in a constant temperature oil bath. Then 0.292 g of I was added and the reaction was monitored by measuring the carbonyl absorbance for the cyclic carbonate at selected time intervals against the solvent blank on the Perkin-Elmer Model 137 spectrophotometer. The half-life for each reaction is given in Table IV.

Reaction of I with α-Toluenethiol (Benzyl Mercaptan).—To 15 ml of xylene at 100° was added 0.292 g of I. After dissolution, 1.0 ml of triethylamine was added, followed by the addition of 4.0 ml of a solution composed of 2.5 ml of α-toluenethiol and 18.5 ml of xylene. The reaction mixture was then placed in an oil bath at 100° and the reaction monitored by removing portions and recording the absorbance at 2000–1570 cm^{-1}.

Reaction of I with Benzylamine.—To a solution of 0.292 g of I in 20 ml of xylene at 100° was added 0.428 g of benzylamine. The reaction mixture was kept at 100° in an oil bath and the reaction monitored by recording the absorbance at 2000–1570 cm^{-1}.

Registry No.—I, 14419-73-9; benzyl alcohol, 100-51-6; α-toluenethiol, 100-53-8; benzylamine, 100-46-9.

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Rearrangements of O and N Acyl and Alkoxycarbonyl Derivatives of *o*-Aminophenol

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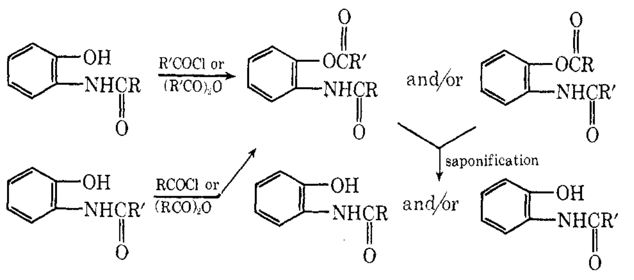
The preparation of several acyl–alkoxycarbonyl O,N derivatives of *o*-aminophenol by both orders of introduction of groups has produced only one isomer, the *N*-alkoxycarbonyl-*O*-acyl derivative, a rearrangement occurring in one of the preparations. Saponification of these derivatives is shown definitely to proceed without rearrangement. Isomeric bisalkoxycarbonyl derivatives were obtained, dependent upon the order of introduction of groups, a result contrary to most previously reported experience with compounds of this type. Furthermore, saponification of these derivatives gave no rearrangements. A mechanism is presented in an attempt to explain these data and most of the data previously reported.

Rearrangements occurring during preparation and saponification of O,N-disubstituted derivatives of *o*-aminophenol are well known (Scheme I). The extensive work involving these diacyl derivatives published by Raiford and coworkers[2] has indicated that, when two different acyl groups are introduced into an *o*-aminophenol, the same diacyl derivative usually is obtained regardless of the order of introduction. Other workers, however, have isolated isomeric pairs of diacyl derivatives.[3,4]

SCHEME I



R and R′ = alkyl or alkoxy group

Studies by Ransom[5] and by Nelson and coworkers[3,4] of derivatives containing an acyl and an alkoxycarbonyl group have shown that only one isomer results, regardless of the order of introduction of groups. Saponification of each of these derivatives has, with one exception,[6] always produced the urethane. These workers, therefore, assumed that the O,N-disubstituted compounds were *N*-alkoxycarbonyl-*O*-acyl derivatives and not the isomeric *N*-acyl-*O*-alkoxycarbonyl derivatives. This proof of structure has, however, become questionable because of the demonstration of LeRosen and Smith[7,8] in an analogous case involving acyl groups that there is a tendency to rearrange during saponification which is exactly the reverse of the tendency to rearrange during the preparation and purification of such compounds. If this is true of the partial rearrangements that they observed, it is at least possible that in the preparations of acyl–alkoxycarbonyl derivatives studied by Nelson and coworkers a complete (or nearly complete) rearrangement may have occurred during the preparation of the compounds, and a reverse rearrangement during saponification, which would have caused wrong structures to be assigned to the disubstituted products.

The theoretical considerations developed by LeRosen and Smith also can be shown to cast doubt upon the assigned structures. Their "principal of minimum charge concentration" would predict that the more stable isomer should be the one that has the more electron-releasing group on the carbonyl group that is attached

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[1] Abstracted in part from the Ph.D. Thesis of C. Ambrosio, The University of Connecticut, 1965.

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